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(54) Title: **KINK RESISTANT MEDICAL TUBES**

(57) Abstract: Kink resistant medical tube, manufactured from a polymer composition comprising a) a random polypropylene copolymer; b) a block copolymer comprising at least two vinyl aromatic polymer blocks and at least one hydrogenated conjugated diene polymer block, wherein the hydrogenated conjugated diene polymer block has a vinyl content before hydrogenation of at least 50 %.

**WO 01/94466 A1**

## KINK RESISTANT MEDICAL TUBES

Background of the invention

The present invention relates to medical tubes that are resistant to kinking when bent and have a commercially acceptable degree of transparency. The invention further relates to polymer compositions that are useful in manufacturing these medical tubes.

Medical tubes are frequently made from plasticized PVC (polyvinylchloride). However, two major disadvantages of the use of plasticized PVC are the driving forces behind the development of alternatives. Firstly, plasticized PVC has an undesired environmental impact, related to the release of dioxins and chlorine, when PVC is incinerated. Secondly, migration of toxic plasticisers, so-called "oestrogene mimics", from plasticized PVC into the human body may have a negative health effect. In addition, plasticized PVC has an insufficient thermal stability to allow for high pressure steam sterilisation in an autoclave.

An alternative for the plasticized PVC is the use of polymer compositions containing polypropylene and an elastomeric block copolymer. These compositions do not contain "oestrogene mimics". Besides the products made therefrom can be heated/molten and used anew in a new application. Additionally these compositions have an improved thermal resistance and can therefore be sterilised by high pressure steam sterilisation in an autoclave.

Kink resistant medical tubes made from a composition containing polypropylene and an elastomeric block copolymer are described in United States patent No. 3865776. This patent relates to kink-resistant

polymeric tubing and a composition therefore. The composition comprises at least five components: a block copolymer of at least two monoalkenylarene polymer blocks and at least one hydrogenated conjugated diene polymer block having a monoalkenylarene content of 28-35 wt% and a molecular weight in the range from 20,000 to 35,000; a block copolymer of at least two monoalkenylarene polymer blocks and at least one hydrogenated conjugated diene polymer block having a monoalkenylarene content of 26-35 wt% and a molecular weight in the range from 8,000 to 155,000; a polypropylene component; a mineral white oil; and a resin component. No specific vinyl content for the hydrogenated conjugated diene polymer blocks is required and no specific type of polypropylene is required. With the described composition a tube having a diameter of about 3/8 inch (about 0.95 cm) can be manufactured that can be bent to a circumference of about nine inches (about 22.86 cm) without kinking. Although with the composition as described in United States patent No. 3865776 a reasonable degree of kinking resistance can be obtained, there is still room for further improvement. Furthermore it would be advantageous if kink-resistant tubes could be prepared from a composition containing less components.

Further polymer compositions containing polypropylene and an hydrogenated elastomeric block copolymer are known from Japanese patent No. 10067894. This patent describes the use of a composition, containing a polypropylene resin and an hydrogenated block copolymer for medical devices to obtain a good flexibility and clarity. The polypropylene resin can be an homopolypropylene polymer, a random polypropylene polymer or a block polypropylene polymer. The hydrogenated block copolymer contains a polyvinyl aromatic block and a polyconjugated diene block wherein the polyconjugated diene block has a high vinyl

content. It will be appreciated that with the term "vinyl content" actually is meant the content of conjugated diene that is polymerised in a 1,2-manner.

According to European Patent No. 0623651, a  
5 transparent and easily processible composition for use in medical devices comprises hydrogenated polystyrene-polybutadiene-polystyrene or polystyrene-polyisoprene-polystyrene block copolymer; random polypropylene  
10 copolymer which contains, as comonomer, ethylene or butylene in concentrations of 2 to 8%; plasticiser oil; and optionally an antistatic. No specific vinyl content for the polybutadiene or polyisoprene block is required.

Japanese patent No. 10067894 and European Patent No. 0623651 do not mention the problem of kinking  
15 resistance for medical tubes. Medical tubes, however, should also be resistant to kinking in addition to good flexibility and clarity. During application, medical tubes should be able to being bent around obstacles, without kinking. Kinking involves more than just  
20 flexibility. Not all flexible tubes behave the same during bending. Some tubes can be bend without kinking, while others kink easily, drastically reducing the cross-sectional area of the tube. In medical tubes, the reduction of flow area can cause severe reduction in the  
25 flow of vital fluids. Therefore the kinking resistance is of essential importance for medical tubes.

Kink resistance is understood to be related to maintaining an increasing stress with increasing elongation. Kinking is not related to the compressive  
30 side when a tube is bent, but to the elongated side. When bending an flexible tube one reaches a certain point where further elongation occurs without resistance, also called the yield point, that is where kinking occurs. A more extensive explanation of kinking can be found in  
35 United States patent No. 3865776.

The object of the present invention is thus to provide medical tubes, which have an improved kinking resistance and still display a commercially attractive degree of clarity or transparency. A further object is to provide a composition for use in the production of these kink-resistant medical tubes.

#### Summary of the invention

The object of the invention is achieved by the following medical tube:

Kink resistant medical tube, manufactured from a polymer composition comprising:

- a) a random polypropylene copolymer;
  - b) a block copolymer comprising at least two vinyl aromatic polymer blocks and at least one hydrogenated conjugated diene polymer block,
- wherein the hydrogenated conjugated diene polymer block has a vinyl content before hydrogenation of at least 50%.

The invention further provides the use of the above mentioned polymer composition for the manufacture of medical devices having kink-resistance.

The applicant has further found that certain polymer compositions are novel and therefore the invention also provides a polymer composition comprising:

- a) a random polypropylene copolymer;
  - b) a block copolymer comprising at least two vinyl aromatic polymer blocks and at least one hydrogenated conjugated diene polymer block,
- wherein the hydrogenated conjugated diene polymer block has a vinyl content before hydrogenation in the range of 60 to 70%.

#### Detailed description of the invention

The kink resistant medical tubes according to the invention can thus be obtained by using a specific polymer composition comprising a random polypropylene copolymer and a specific block copolymer.

Component a) of the polymer composition is a random polypropylene copolymer or a mixture of random polypropylene copolymers. By a random polypropylene copolymer is understood a polymer wherein propylene monomers and one or more non-propylene alkylene co-monomers are present in a statistically random manner in the macromolecule. Suitable examples of co-monomers are ethylene, 1-butylene, 1-pentylene, 1-hexylene, 4-methyl-1-pentylene, 2-methylpropylene, 3-methyl-1-pentylene and 5-methyl-1-hexylene or mixtures of these co-monomers. Preferred co-monomers are ethylene and 1-butylene. The amount of co-monomer included may vary between wide ranges but is suitably in the range from 0.5 to 10 wt%, preferably in the range from 2 to 8 wt% and more preferably in the range from 2 to 5 wt%. Most preferably the random polypropylene copolymer is a random polypropylene copolymer containing from 2 to 8 wt% of ethylene or 1-butylene. To improve the transparency of the blend, the random polypropylene polymer can further contain a nucleating agent.

The random polypropylene copolymer should have a melt flow rate in the range of 1 to 100 dg/min, preferably between 10 and 13 dg/min. The melt flow rate is measured according to ASTM D1238.

Component b) of the polymer composition is a block copolymer or a mixture of block copolymers. The block copolymer(s) may be either linear, with a formula  $(A-B)_n-A$  or  $(A-B)_m$ , or branched, with a formula  $(A-B)_pX$ . In these formulae A stands for a monovinyl aromatic polymer block; B stands for a hydrogenated conjugated diene polymer block; X stands for a coupling agent; n is 1 or more, preferably from 1 to 3, and most preferably 1; m is more than 1, preferably from 2 to 4 and most preferably 2; and p is more than 1, preferably from 2 to 10, more preferably from 2 to 5, most preferably from 2

to 4. Preferably component b) comprises a linear triblock copolymer (ABA). Component b) may further contain some amount of diblock (AB), to the extent that it does not interfere with the properties of the block copolymer component as a whole. The amount of diblock copolymer should be less than 50 wt% of the total block copolymer component, and more suitably be less than 30 wt%, most suitably be less than 15 wt%. Preferably component b) contains no or essentially no diblock copolymer.

10       The prepared block copolymer may have a tapered block structure. Each block should contain predominantly only one component, A or B. The presence of the other component than the predominant one should be less than 5 wt%, more preferably less than 2 wt%. Most preferably  
15       each block contains only one or essentially only one component, i.e. A or B.

      The block copolymers, which are useful in the polymer composition according to the present invention, may be prepared by any method known in the art including the  
20       well known full sequential polymerisation method, optionally in combination with reinitiation, and the coupling method, as illustrated in e.g. U.S. Patents Nos. 3,231,635; 3,251,905; 3,390,207; 3,598,887 and 4,219,627 and EP 0413294 A2, 0387671 B1, 0636654 A1,  
25       WO 04/22931. The block copolymer may therefore, for example, be prepared by coupling at least two diblock copolymer molecules AB together.

      The coupling agent may be any di- or polyfunctional coupling agent known in the art, for example, dibromo-  
30       ethane, silicon tetrachloride, diethyl adipate, divinylbenzene, dimethyldichlorosilane, methyl dichlorosilane. Particularly preferred in such a preparation route is the use of non-halogen containing coupling agents, for example gamma-glycidoxypyrpyl-trimethoxysilane, and  
35       diglycidylether of bisphenol A.



Suitable vinyl aromatic compounds include those having 8 to 20 carbon atoms and include styrene, o-methylstyrene, p-methylstyrene, p-tert-butylstyrene, 2,4-dimethylstyrene,  $\alpha$ -methylstyrene, vinylnaphthalene, vinyltoluene and vinylxylene, or mixtures thereof. Preferred monovinyl aromatic compounds are styrene, alpha-methylstyrene and para-methylstyrene, styrene being the most preferred. Although the average molecular weight of the vinyl aromatic polymer blocks is not restricted, the number average molecular weight is preferably within the range of 2,500 to 20,000.

Suitable conjugated dienes include those having from 4 to 8 carbon atoms, for example 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene and 1,3-hexadiene. Mixture of such dienes may also be used. Preferred conjugated dienes are 1,3-butadiene and isoprene. Of these, 1,3-butadiene is most preferred, because it leads to a polymer composition having advantageous low temperature properties, such as a good flexibility at low temperatures. For example, a polymer composition comprising polystyrene-hydrogenated polyisoprene - polystyrene and random polypropylene polymer in a weight ratio of 50:50 becomes brittle below temperatures of 10 °C, whereas a similar polymer composition with hydrogenated polybutadiene as conjugated diene block maintains a sufficient degree of flexibility even below temperatures of -25 °C. Often medical tubes and the products contained in them require storage at low temperatures. In these cases low temperature properties of the polymer composition are of essential importance. Furthermore butadiene is preferred for economical reasons, since the costs for obtaining butadiene are lower than for isoprene.

The conjugated diene polymer block should have a vinyl content before hydrogenation of at least 50%, i.e.

the conjugated diene polymer block should have a vinyl content before hydrogenation of 50% or more. The optimal vinyl content may vary with the conjugated diene used and the amount of hydrogenated block copolymer used in the composition. Polybutadiene block(s) preferably have a vinyl content before hydrogenation of at least 60%, and more preferably of at least 65%. For cost-reasons increasing the vinyl content beyond 70% is not preferred. Applicant has found that increasing the vinyl content further does not increase kinking resistance or transparency to such an extent that the higher costs made to obtain this increased vinyl content can be justified. The vinyl content of the conjugated diene block(s) is therefore preferably less than 70%.

Techniques to control the vinyl content of the conjugated diene portion are well known and may involve the use of polar compounds such as ethers, amines and other Lewis bases and more in particular those selected from the group consisting of dialkylethers of glycols. Most preferred modifiers are selected from dialkyl ether of ethylene glycol containing the same or different terminal alkoxy groups and optionally bearing an alkyl substituent on the ethylene radical, such as monoglyme, diglyme, diethoxyethane, 1,2-diethoxy-propane, 1-ethoxy-2,2-tert-butoxyethane, of which 1,2-diethoxypropane is most preferred.

Although the average molecular weight of the conjugated diene blocks is not restricted, the number average molecular weight is preferably within the range of 10,000 to 150,000.

The number average molecular weights referred to in this specification and claims for component b) or constituents of component b) are measured with gel permeation chromatography (GPC) using poly(styrene) calibration standards (according to ASTM 3536). GPC is a

well known method wherein polymers are separated according to molecular size, the largest molecule eluting first. The chromatograph is calibrated using commercially available polystyrene molecular weight standards. The  
5 molecular weight of other (block) polypolymers is expressed as styrene equivalent molecular weight.

After preparation, hydrogenation of the block copolymer may be accomplished using any of the methods known in the prior art. The hydrogenation will preferably  
10 be selective hydrogenation accomplished using a method such as those taught in U.S. Patent Nos. 3,494,942; 3,634,549; 3,670,054; 3,700,633 and Re 27,145, which are incorporated herein by reference. Most preferably, selective hydrogenation will be accomplished using one of  
15 the processes taught in U.S. Patent No. 3,700,633. These hydrogenation processes involve the use of a suitable catalyst, particularly a catalyst or catalyst precursor comprising an iron group metal compound. In the methods described in the foregoing patent documents, the catalyst  
20 is prepared by combining an iron group metal, particularly a nickel or cobalt compound with a suitable reducing agent such as an aluminium alkyl. The preferred iron group metal compounds are carboxylates and alkoxides.

25 The block copolymer is preferably selectively hydrogenated, thereby converting (hydrogenating) at least 80 percent, more preferably more than 98 percent and most preferably more than 99% of the initial unsaturation in the conjugated diene polymer block. Preferably, less than  
30 10 percent and most preferably less than 2 percent of the initial unsaturation in the vinyl aromatic polymer blocks is hydrogenated to obtain the maximum benefits of hydrogenation.

The total number average molecular weight of the  
35 hydrogenated block copolymer is preferably within the

range from 15,000 to 200,000, and more preferably within the range from 50,000 to 150,000 for linear block copolymers and within the range from 50,000 to 200,000 for branched block copolymers.

5       The vinyl aromatic content of the (total) block copolymer should be in the range from 10 to 40 wt% and is preferably in the range from 10-25 wt%. If the vinyl aromatic content exceeds 40% by weight, then the melt viscosity of a block copolymer is too high and it will be  
10       difficult to mix the block copolymer uniformly with the polypropylene. If the vinyl aromatic content is less than 10% by weight, the mechanical strength of the block copolymer is inadequate.

15       The weight ratio between component a) of the polymer composition, i.e. the random polypropylene copolymer(s), and component b) of the polymer composition, i.e. the block copolymer(s), preferably lies in the range from 80:20 to 30:70 and is more preferably in the range from 60:40 to 50:50.

20       The polymer composition may also, optionally, contain various additives, such as antioxidants, ultraviolet absorbers, light stabilisers or colouring agents. Preferably the amount of these additives present in the polymer composition is not more than 5 weight parts per  
25       100 weight parts of random polypropylene and block copolymer. Medicinal oils are also frequently applied, as plastizer. Preferably the amount of medicinal oil present in a polymer composition is not more than 50 weight parts on 100 weight parts of random polypropylene and block  
30       copolymer, more preferably not more than 25 weight parts. Most preferably the polymer composition contains no or little medicinal oil.

35       The polymer composition can be prepared using kneading machines, such as a single screw extruder, a twin screw extruder, a Banbury mixer or a roll. The kink

resistant medical tubes can be prepared from the obtained polymer composition by arbitrary methods such as injection moulding or extrusion moulding. The obtained kink resistant medical tubes are excellent in kink-resistance, while still having commercially attractive transparency. Suitable inner diameters for the obtained kink resistant medical tubes are in the range from 0.1 to 2.0 cm, more suitably in the range from 0.3 to 1.0 cm. Suitable thicknesses of the medical tube wall are in the range from 0.1 to 5 mm. Examples of the medical tubes include urinary tubes, gas delivery tubes, blood tubing and infusion tubes.

The polymer composition as described above can further be advantageously used in the manufacture of medical devices having kink resistance, other than medical tubes, such as for example kink resistant connectors between medical tubes, catheters or (blood) bags.

Certain polymer compositions useful in the manufacture of kink-resistant medical tubes are novel and the invention therefore also provides a polymer composition comprising:

- a) a random polypropylene copolymer;
  - b) a block copolymer comprising at least two vinyl aromatic polymer blocks and at least one hydrogenated conjugated diene polymer block,
- wherein the hydrogenated conjugated diene polymer block has a vinyl content before hydrogenation in the range from 60 to 70%.

Although the conjugated diene can be any of the conjugated dienes mentioned hereinbefore, isoprene or butadiene are preferred and butadiene is especially preferred for the hereinabove mentioned reasons. For a polymer composition comprising butadiene in the conjugated diene polymer block(s) a vinyl content in the

range from 65 to 70% before hydrogenation is preferred. Further preferences for the polymer composition are as described hereinbefore.

5 The invention will now be illustrated by the following non-limiting examples.

Examples 1-5 and comparative examples A and B

Polymer compositions 1-5 and A and B were prepared by mixing random polypropylene polymer (PP) (Montell grade EP2X29GK) with various polystyrene-hydrogenated poly-  
10 butadiene-polystyrene block copolymers, varying in vinyl content in the polybutadiene block before hydrogenation, in a weight ratio of 70:30. The polystyrene- hydrogenated polybutadiene-polystyrene block copolymers had an  
15 molecular weight determined by GPC of about 100,000, were hydrogenated to a degree of more than 99% and contained about 20 wt% styrene. The final composition was  
sterilised by high pressure steam sterilisation in an autoclave at 120 °C during 2 hours. Of these compositions  
20 the glass transition temperature (Tg) of the polystyrene- hydrogenated polybutadiene-polystyrene block copolymers before mixing with the polypropylene polymer; the Tg of the resultant composition; the transparency of the  
composition and kinking of a tube prepared with the composition was determined. The Tg's were determined by  
25 DMA (Dynamic mechanical analysis) with a Rheometrics RDS-2, heating at 10 °C/min, frequency 10 Hz, strain 1% on rectangular samples. Transparency was determined visually, on injection moulded test-plates and on  
extruded tubes 1 hour after the sterilisation test at  
30 120 °C during 2 hour. Kinking resistance was measured on an extrusion moulded tube having an outer diameter of 7 mm and an inner diameter of 5 mm. Kinking of the tube was determined by the hand test described in United  
States patent No. 3865776. The described hand test  
35 consists of bringing the ends of a flexible tube of

appropriate length together and parallel shortening the loop formed until kinking occurs and measuring the outer circumference of the loop portion of the tube. The value given represents the circumference of the loop portion of the tube where kinking starts.

Results of the tests can be found in table 1.

#### Example 6

Polymer composition 6 was prepared by mixing random polypropylene polymer (Montell grade EP2X29GK) with a hydrogenated polystyrene-polyisoprene-polystyrene block copolymer (Kuraray grade HVS-03) having a vinyl content in the polyisoprene block before hydrogenation of about 50%, in a weight ratio of 70:30. Results of the tests can be found in table 1.

#### Comparative example C

The Polymer composition for comparative example C was prepared by mixing random polypropylene polymer (Montell grade EP2X29GK) with a polystyrene- hydrogenated random polybutadiene/styrene-polystyrene block copolymer, having a vinyl content in the midblock of about 50% and an overall styrene content of 40 wt%, of which 20 wt% is contained in the midblock, in a weight ratio of 70:30. Results of the tests can be found in table 1.

Table 1: Variation of the vinyl content in the conjugated diene polymer block of the block copolymer.

Example	Vinyl content of the conjugated diene polymer block before hydro-generation	Tg of the block copolymer (°C)	Tg of the composition of block copolymer and PP (°C)	Transparency of the composition tube (cm)	Kinking of the tube (cm)
A	40	-52	-52/0	moderate	17-19
B	45	-51	-51/0	moderate	17-19
1	60	-48	-48/0	good	15-17
2	65	-47	-42/0	high	13-15
3	69	-45	-38/0	excellent	13-15
4	73	-43	-34/0	excellent	13-15
5	78	-38	-26/0	excellent	13-15
6 (Kuraray)	50	-18	0 (single peak)	excellent	13-15
C (S-EB/S-S)	50	-35	-35/0	non-transparent	13-15



From the results in table 1 it can be seen that for good transparency and kinking resistance of the polymer composition comprising a polystyrene-hydrogenated polybutadiene-polystyrene block copolymer, a vinyl content in the polybutadiene block before hydrogenation of at least 50% is needed. Example 2 shows that the kinking resistance is further improved when the vinyl content is increased to 65%. Examples 3, 4 and 5 show that vinyl contents higher than 69% do not further improve the kinking resistance or the transparency. Example 6 shows that good kinking resistance can also be obtained with a polymer composition comprising a hydrogenated polystyrene-polyisoprene-polystyrene block copolymer with a vinyl content of 50% in the polyisoprene block before hydrogenation. However, as shown by the Tg's, the composition comprising this hydrogenated polystyrene-polyisoprene-polystyrene block copolymer has a worse application temperature range. Due to the very high Tg, the blend becomes brittle below 10 °C.

Comparative example C shows that although a good kinking resistance can be obtained with a polystyrene-random polybutadiene/styrene-polystyrene block copolymer, the transparency of such a composition is unacceptable. Examples 7-11 and comparative example D

The polystyrene- hydrogenated polybutadiene-polystyrene block copolymer used in example 3, with a vinyl content of 69%, was mixed with random polypropylene polymer (Montell grade EP2X29GK) in several weight ratio's. The Tg of the block copolymer and the resultant polymer composition, the transparency and the kinking resistance were tested. In an comparative example also the pure random polypropylene polymer, without any block copolymer was tested. The results can be found in table 2. As can be seen from these results, both transparency as well as kinking resistance improve upon

mixing with the block copolymer and good results can be obtained within a wide range of random polypropylene polymer/block copolymer weight ratio's.

Comparative example E

- 5           The polystyrene- hydrogenated polybutadiene-  
polystyrene block copolymer used in example 1, with a  
vinyl content of 40%, was mixed with random polypropylene  
polymer (Montell grade EP2X29GK) with in a weight ratio  
of 50:50. The Tg of the block copolymer and the resultant  
10 polymer composition, the transparency and the kinking  
resistance were tested. The results can be found in  
table 2. As can be seen from these results, the  
transparency of the composition is unacceptable.

Table 2: Effect of blend ratio random polypropylene polymer (PP)/block copolymer.

Example	Ratio PP/block copolymer	Tg of the block copolymer (°C)	Tg of the composition of block copolymer and PP (°C)	Transparency of the composition	Kinking of the tube (cm)
D	100/0	-	0	moderate	21-23
9	70/30	-45	-38/0	excellent	13-15
10	60/40	-45	-36/0	excellent	11-13
11	50/50	-45	-34/0	excellent	10-11
12	40/60	-45	-30/0	excellent	9-10
13	30/70	-45	-25/0	excellent	7-9
E	50/50	-52	-50/0	moderate	14-15

Examples 12, 13 and comparative example F

In example 12 and 13 the polystyrene-hydrogenated polybutadiene-polystyrene block copolymer used in example 3, with a vinyl content of 69%, was mixed with two different random polypropylene copolymer (Montell grade EP2X29GK and Montell grade PLZ 886) in a weight ratio of 50:50. The Montell grade EP2X29GK polypropylene copolymer also contains a nucleating agent whereas the Montell grade PLZ 886 polypropylene copolymer does not.

As a comparative example the polystyrene-hydrogenated polybutadiene-polystyrene block copolymer used in example 3, with a vinyl content of 69%, was mixed with a non-random soft polypropylene polymer (Adflex F200) in a weight ratio of 50:50. Results of the tests can be found in table 3. The results show that the composition based on EP2x29GK (Montell) has an improved transparency over the composition based on PLZ886 (Montell), because EP2x29GK (Montell) contains a nucleating agent. The use of a non-random soft polypropylene results in unacceptable low transparency and non-measurable kink resistance.

Compositions 1-14 and A-E, but not composition F, were able to withstand sterilisation at 121 °C during 2 hours, without permanent deformation occurring and with full recovery of transparency within 1 hour after sterilisation. Because of the deformation occurring during sterilisation, the kinking resistance of the composition containing Adflex F200 (example F) was not measurable.

The results can be found in table 3.

Table 3: Effect of the PP-type

Example	polypropylene polymer	Tg of the block copolymer (°C)	Tg of the composition of block copolymer and PP (°C)	Transparency of the composition	Kinking of the tube (cm)
12	EP 2x29 GK (Montell)	-45	-34/0	excellent	10-11
13	PLZ 886 (Montell)	-45	-32/0	very high	10-11
F	Adflex F200 (soft PP, Montell)	-45	-25 (single peak)	non-transparent	non-measurable

Example 14

To 50 weight parts of polypropylene (EP2x29GK) and 33.3 weight parts of the polystyrene-hydrogenated polybutadiene-polystyrene block copolymer used in example 3, with a vinyl content of 69%, 16.7 weight parts of an medicinal oil (Primol 352, FDA and medical approved oil) were added. It was found that the composition had a Tg of -40/-10, an excellent transparency and kinking of the tube occurred at 10-11 cm. These results show that medicinal oils can be added to the polymer composition while still an excellent transparency and kinking resistance can be obtained.

C L A I M S

1. Kink resistant medical tube, manufactured from a polymer composition comprising
  - a) a random polypropylene copolymer;
  - b) a block copolymer comprising at least two vinyl aromatic polymer blocks and at least one hydrogenated conjugated diene polymer block,wherein the hydrogenated conjugated diene polymer block has a vinyl content before hydrogenation of at least 50%.  
5
2. Kink resistant medical tube according to claim 1,  
10 wherein the random polypropylene copolymer in the polymer composition contains from 0.5 to 10 wt% of ethylene or butylene.
3. Kink resistant medical tube according to claim 1 or 2, wherein the block copolymer in the polymer composition  
15 comprises a linear triblock copolymer of the structure ABA, wherein A stands for a monovinyl aromatic polymer block and B stands for a hydrogenated conjugated diene polymer block.
4. Kink resistant medical tube according to any one of  
20 claims 1 to 3, wherein the hydrogenated conjugated diene polymer(s) in the polymer composition is polybutadiene.
5. Kink resistant medical tube according to claim 4,  
wherein the polybutadiene block(s) of the block copolymer in the polymer composition has a vinyl content in the  
25 range from 60 to 70% before hydrogenation.
6. Kink resistant medical tube according to anyone of claims 1-5, wherein the weight ratio between random polypropylene copolymer and block copolymer in the polymer composition ranges from 80:20 to 30:70.

7. Kink resistant medical tube according to anyone of claims 1-6, wherein an medicinal oil is added in the polymer composition.

8. Use of a polymer composition comprising

- 5 a) a random polypropylene copolymer;  
b) a block copolymer comprising at least two vinyl aromatic polymer blocks and at least one hydrogenated conjugated diene polymer block,  
10 wherein the hydrogenated conjugated diene polymer block has a vinyl content before hydrogenation of at least 50% for the manufacture of medical devices having kink-resistance.

9. Polymer composition comprising:

- 15 a) a random polypropylene copolymer;  
b) a block copolymer comprising at least two vinyl aromatic polymer blocks and at least one hydrogenated conjugated diene polymer block,  
20 wherein the hydrogenated conjugated diene polymer block has a vinyl content in the range from 60 to 70% before hydrogenation.

10. Composition according to claim 11, wherein the hydrogenated conjugated diene polymer block of the block copolymer is a polybutadiene block with a vinyl content in the range from 65 to 70% before hydrogenation.



# INTERNATIONAL SEARCH REPORT

ational Application No

PCT/EP 01/06467

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L53/02 C08L23/10 A61L29/14 A61L29/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L A61L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI Section Ch, Week 199820 Derwent Publications Ltd., London, GB; Class A18, AN 1998-225233 XP002180888 &amp; JP 10 067894 A (KURARAY CO LTD), 10 March 1998 (1998-03-10) cited in the application abstract</p>	<p>1,3-6, 8-10</p>
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
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- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- \*G\* document member of the same patent family

Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

ational Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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